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INTERNAL REPORT

METHOD FOR TREATING PVT DATA FROM A BURNETT

COMPRESSIBILITY APPARATUS

BY

Robert E. Barieau

B. J. Dalton

BRANCH Fundamental Research

PROJECT NO. 4335

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METHOD FOR TREATING PVT DATA FROM A BURNETT COMPRESSIBILITY APPARATUS

by

Robert E. Barieau[1/] and B. J. Dalton[2/]

ABSTRACT

This report describes the method employed by the Helium Research Center for treating PVT data from a Burnett compressibility apparatus so that the compressibility is obtained as a function of pressure or molal density. In addition, formulas are given for determining the variances of all calculated quantities and for calculating variances and covariances of all constants evaluated.

INTRODUCTION

In 1936, Burnett (3)[3/] announced his method for obtaining PVT data on gases which eliminates the necessity of making any mass or volume measurements. The only data observed are the temperature of the isotherm being studied and a series of pressures and expansion numbers.

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3/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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The Burnett apparatus consists of two thermostated containers, connected through a pressure valve, and a pressure gage. The first container is filled with gas to some high pressure and the initial pressure is determined. Then this same mass of gas is expanded into the second container, which has previously been evacuated, and the two containers are allowed to come to equilibrium. The pressure is then determined, the first container is isolated, and the second container is again evacuated. This process is repeated a number of times so that a series of pressures and expansion numbers are obtained.

This report describes the way such data are treated at the Helium Research Center, Bureau of Mines, so that the compressibility is obtained as a function of the pressure or of the molal density. In addition, formulas are given for determining the variances of all calculated quantities and for calculating the variances and covariances of all constants evaluated.

The method and the relationships outlined in this report for treating PVT data from a Burnett compressibility apparatus have been developed for the compressibility being a function of two parameters, B and C. The extension of this method to the evaluation of more parameters should be obvious.

THEORY OF THE BURNETT METHOD

When the first container is filled to pressure P_o, the following exact equation applies

$$P_o V_{1,o} = nRTZ_o \qquad (1)$$

where

P_o is the initial pressure,

$V_{1,o}$ is the volume of the first container when filled to the pressure P_o,

n is the number of moles of gas,

R is the universal gas constant,

T is the absolute thermodynamic temperature, and

Z_o is the compressibility factor of the gas at pressure P_o and is defined by equation (1).

On expanding the gas into the second container, the following exact equation applies

$$P_1 V_{2,1} = nRTZ_1 \qquad (2)$$

where

P_1 is the equilibrium pressure after the first expansion,

$V_{2,1}$ is the volume of the first and second containers under the pressure P_1, and

Z_1 is the compressibility factor of the gas at pressure P_1 and is defined by equation (2).

Dividing equation (2) by equation (1), we have

$$\frac{Z_1}{Z_o} = \frac{P_1 V_{2,1}}{P_o V_{1,o}} \qquad (3)$$

or

$$Z_1 = \frac{Z_o}{P_o}\frac{V_{2,1}}{V_{1,o}}P_1 \tag{4}$$

Let

$$N_1 = \frac{V_{2,1}}{V_{1,o}} \tag{5}$$

N_1 is called the volume ratio of the first expansion. This will be a function of the pressure because of the change in volume of the containers with pressure. If α is the pressure coefficient of the volume of the two containers, and β is the pressure coefficient of the first container, we have

$$V_{1,o} = V_1^o\left(1 + \beta P_o\right) \tag{6}$$

$$V_{2,1} = V_2^o\left(1 + \alpha P_1\right) \tag{7}$$

where V_1^o is the volume of container 1 under zero pressure, and V_2^o is the volume of the two containers under zero pressure. Substituting equations (6) and (7) into equation (5), we have

$$N_1 = \frac{V_2^o\left(1 + \alpha P_1\right)}{V_1^o\left(1 + \beta P_o\right)} \tag{8}$$

We now let

$$N_{P=0} = \frac{V_2^o}{V_1^o} \tag{9}$$

where $N_{P=0}$ is then the volume ratio at zero pressure. Substituting equations (8) and (9) into equation (4), we have

$$Z_1 = \frac{Z_o}{P_o} N_{P=0}\left(\frac{1 + \alpha P_1}{1 + \beta P_o}\right)P_1 \tag{10}$$

A similar equation holds for the second expansion

$$Z_2 = \frac{Z_1}{P_1} N_{P=0}\left(\frac{1 + \alpha P_2}{1 + \beta P_1}\right)P_2 \tag{11}$$

If we multiply equation (10) by equation (11), we find

$$Z_2 = \frac{Z_o}{P_o} N^2_{P=0} \frac{(1 + \alpha P_1)(1 + \alpha P_2)}{(1 + \beta P_o)(1 + \beta P_1)} P_2 \tag{12}$$

The expression for the r^{th} expansion is

$$Z_r = \frac{Z_{r-1}}{P_{r-1}} N_{P=0}\left(\frac{1 + \alpha P_r}{1 + \beta P_{r-1}}\right)P_r \tag{13}$$

Multiplying Z_r by Z_{r-1}, Z_{r-2}, ..., Z_1, we find

$$Z_r = \frac{Z_o}{P_o} N^r_{P=0} f_r P_r \tag{14}$$

where

$$f_r = \frac{(1 + \alpha P_1)(1 + \alpha P_2) \ \ldots \ (1 + \alpha P_r)}{(1 + \beta P_o)(1 + \beta P_1) \ \ldots \ (1 + \beta P_{r-1})} \tag{15}$$

The problem of treating data obtained by the Burnett method is to evaluate the constants that appear in the expression for the compressibility, Z, and to also evaluate, simultaneously, the volume ratio, $N_{P=0}$, that appears in equation (14). We evaluate these constants by the general non-linear least squares technique that we have developed for this particular purpose (1).

METHOD OF OBTAINING THE LEAST SQUARES VALUES OF THE CONSTANTS WHICH APPEAR IN THE FUNDAMENTAL EQUATION FOR THE BURNETT METHOD

For the Burnett method, we define

$$F = F(r, P_r, B, C, N_{P=0})$$

$$= Z_r - \frac{Z_o}{P_o} N^r_{P=0} f_r P_r = 0 \qquad (16)$$

In equation (16), Z_r can be an explicit function of either the pressure, P_r, or the molal density, ρ_r, in which case Z_r is to be considered an implicit function of P_r through the equation

$$\rho_r = \frac{P_r}{RTZ_r} \qquad (17)$$

Z_r and Z_o of equation (16) are functions of the parameters B and C which are to be evaluated but are not functions of $N_{P=0}$. f_r is a function of all of the pressures P_o, P_1 ..., P_r, it being assumed that α and β, which appear in the expression for f_r, have been independently determined and are exactly known.

In equation (16), we assume that the expansion number, r, is exactly known. We assume random errors only in the observed P_r's, and that they are normally distributed.

Now because of random errors in the observed P_r's, when $P_{r(obs)}$ is substituted in equation (16), F will not reduce exactly to zero. Let F_r be the value of F when the observed values of r and P_r are substituted in equation (16). Thus

$$F_r = F(r, P_{r(obs)}, B, C, N_{P=0}) \tag{18}$$

Now equation (16) can be solved for a calculated P_r so that F reduces to zero. Thus

$$F = F(r, P_{r(calc)}, B, C, N_{P=0}) = 0 \tag{19}$$

To calculate $P_{r(calc)}$, we use the Newton-Raphson method and an iterative technique. We first calculate $\left(\frac{\partial F}{\partial P_r}\right)_{r,B,C,N_{P=0}}$ at $P_{r(obs)}$. Then as a first approximation, we take

$$P_{r(obs)} - P_{r(calc)_1} = \frac{F_r}{\left(\frac{\partial F}{\partial P_r}\right)_{r,B,C,N_{P=0}}} \tag{20}$$

The solution of equation (20) gives $P_{r(calc)_1}$, which is the first approximation of $P_{r(calc)}$. This value is then substituted into equation (16) and, if equation (16) is not exactly satisfied, then $P_{r(calc)_1}$ is not the exact answer, so we let F_{r_1} be the numerical

value of F at $P_{r(calc)_1}$

$$F_{r_1} = F(r, P_{r(calc)_1}, B, C, N_{P=0}) \tag{21}$$

We then evaluate $\left(\frac{\partial F}{\partial P_r}\right)_{r,B,C,N_{P=0}}$ at $P_{r(calc)_1}$ and, as a second approximation, we take

$$P_{r(calc)_1} - P_{r(calc)_2} = \frac{F_{r_1}}{\left(\frac{\partial F}{\partial P_r}\right)_{r,B,C,N_{P=0}}} \tag{22}$$

We repeat the iteration until equation (19) is satisfied to within any amount we wish to specify.

We then define

$$Y_r = P_{r(obs)} - P_{r(calc)} \tag{23}$$

Now Y_r, the residual of $P_{r(obs)}$, is the difference between the observed and calculated values. This is not the true random error in our observed P_r because we do not know the true value of $P_{r(obs)}$. However, we can maximize the probability that the Y_r's are equal to the true random errors, and this is just what the principle of least squares does. The principle of least squares says that we maximize the probability that the Y_r's represent the true random errors by minimizing the sum of the weighted squares of the residuals. Thus, we should minimize the function

$$R = \sum_{r=1}^{n} W_{P_{r(obs)}} (Y_r)^2 \tag{24}$$

and evaluate $N_{P=0}$, B, and C so that

$$\left(\frac{\partial R}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} = 2\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} = 0 \qquad (25)$$

$$\left(\frac{\partial R}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} = 2\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} = 0 \qquad (26)$$

$$\left(\frac{\partial R}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} = 2\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} = 0 \qquad (27)$$

In equation (24), $W_{P_{r(obs)}}$ is the weight to be assigned to the observed P_r. If the $P_{r(obs)}$'s all have the same precision index, then they will have the same weight and $W_{P_{r(obs)}} = 1$. If the $P_{r(obs)}$'s do not all have the same precision index, then

$$W_{P_{r(obs)}} = \frac{L^2}{S^2_{P_{r(obs)}}} \qquad (28)$$

where L is a constant and $S^2_{P_{r(obs)}}$ is the variance of $P_{r(obs)}$.

In a particular problem, it may be necessary to assume $W_{P_{r(obs)}} = 1$ in the beginning. However, if this is done the residuals, $Y_r = [P_{r(obs)} - P_{r(calc)}]$, should be examined to see if there is any statistical evidence for the residuals squared being a function of $P_{r(obs)}$. Any assumption as to the variance being a function of $P_{r(obs)}$ can always be checked by examining the residuals. In any event, $W_{P_{r(obs)}}$ is not a function of the constants to be evaluated.

In order to evaluate $N_{P=0}$, B, C, we need to linearize equations (25), (26), and (27) with respect to the undetermined constants. A truncated Taylor's series expansion can be used to do this. The normal equations, written in linearized form, are

$$a_1 \Delta B + b_1 \Delta C + c_1 \Delta N_{P=0} = m_1 \qquad (29)$$

$$a_2 \Delta B + b_2 \Delta C + c_2 \Delta N_{P=0} = m_2 \qquad (30)$$

$$a_3 \Delta B + b_3 \Delta C + c_3 \Delta N_{P=0} = m_3 \qquad (31)$$

Equations (29), (30), and (31) result from expanding Y_r, $\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}$, $\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}}$, and $\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C}$ about an approximate solution, Y_r^o, ignoring second and higher order derivatives. The quantities ΔB, ΔC, $\Delta N_{P=0}$ are defined as

$$\left.\begin{aligned} \Delta B &= B - B_o \\ \Delta C &= C - C_o \\ \Delta N_{P=0} &= N_{P=0} - (N_{P=0})_o \end{aligned}\right\} \qquad (32)$$

where B, C, $N_{P=0}$ are the undetermined constants and B_o, C_o, $(N_{P=0})_o$ are approximate values for these quantities.

The a's, b's, c's, and m's appearing in the linearized normal equations are

$$a_1 = \sum_{r=1}^{n} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_r}{\partial B}\right)^{o^2}_{r,P_{r(obs)},C,N_{P=0}} + Y_r^o \left(\frac{\partial^2 Y_r}{\partial B^2}\right)^{o}_{r,P_{r(obs)},C,N_{P=0}} \right] \qquad (33)$$

$$a_2 = b_1 = \left[\begin{array}{l} \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)^{o}_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial C}\right)^{o}_{r,P_{r(obs)},B,N_{P=0}} \\ + \sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial^2 Y_r}{\partial B \partial C}\right)^{o}_{r,P_{r(obs)},N_{P=0}} \end{array}\right] \quad (34)$$

$$a_3 = c_1 = \left[\begin{array}{l} \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)^{o}_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},B,C} \\ + \sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial^2 Y_r}{\partial B \partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},C} \end{array}\right] \quad (35)$$

$$b_2 = \sum_{r=1}^{n} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_r}{\partial C}\right)^{o^2}_{r,P_{r(obs)},B,N_{P=0}} + Y_r^o \left(\frac{\partial^2 Y_r}{\partial C^2}\right)^{o}_{r,P_{r(obs)},B,N_{P=0}}\right] \quad (36)$$

$$b_3 = c_2 = \left[\begin{array}{l} \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)^{o}_{r,P_{r(obs)},B,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},B,C} \\ + \sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial^2 Y_r}{\partial C \partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},B} \end{array}\right] \quad (37)$$

$$c_3 = \sum_{r=1}^{n} W_{P_{r(obs)}} \left[\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^{o^2}_{r,P_{r(obs)},B,C} + Y_r^o \left(\frac{\partial^2 Y_r}{\partial N_{P=0}^2}\right)^{o}_{r,P_{r(obs)},B,C}\right] \quad (38)$$

$$m_1 = -\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial Y_r}{\partial B}\right)^o_{r,P_{r(obs)},C,N_{P=0}} \tag{39}$$

$$m_2 = -\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial Y_r}{\partial C}\right)^o_{r,P_{r(obs)},B,N_{P=0}} \tag{40}$$

$$m_3 = -\sum_{r=1}^{n} W_{P_{r(obs)}} Y_r^o \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^o_{r,P_{r(obs)},B,C} \tag{41}$$

where

$$\left(\frac{\partial Y_r}{\partial B}\right)^o_{r,P_{r(obs)},C,N_{P=0}} = \frac{(\partial F/\partial B)^o_{r,P_{r(calc)},C,N_{P=0}}}{(\partial F/\partial P_{r(calc)})^o_{r,B,C,N_{P=0}}} \tag{42}$$

$$\left(\frac{\partial Y_r}{\partial C}\right)^o_{r,P_{r(obs)},B,N_{P=0}} = \frac{(\partial F/\partial C)^o_{r,P_{r(calc)},B,N_{P=0}}}{(\partial F/\partial P_{r(calc)})^o_{r,B,C,N_{P=0}}} \tag{43}$$

$$\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^o_{r,P_{r(obs)},B,C} = \frac{(\partial F/\partial N_{P=0})^o_{r,P_{r(calc)},B,C}}{(\partial F/\partial P_{r(calc)})^o_{r,B,C,N_{P=0}}} \tag{44}$$

$$\left(\frac{\partial^2 Y_r}{\partial B^2}\right)^o_{r,P_{r(obs)},C,N_{P=0}} = \left[\frac{\left(\frac{\partial^2 F}{\partial B^2}\right)^o_{r,P_{r(calc)},C,N_{P=0}}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}} - \frac{2\left(\frac{\partial^2 F}{\partial B \partial P_{r(calc)}}\right)^o_{r,C,N_{P=0}} \left(\frac{\partial F}{\partial B}\right)^o_{r,P_{r(calc)},C,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\frac{\partial F}{\partial B}\right)^{o^2}_{r,P_{r(calc)},C,N_{P=0}} \left(\frac{\partial^2 F}{\partial P^2_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^3} \right] \tag{45}$$

$$\left(\frac{\partial^2 Y_r}{\partial C^2}\right)^o_{r,P_{r(obs)},B,N_{P=0}} = \left[\frac{\left(\frac{\partial^2 F}{\partial C^2}\right)^o_{r,P_{r(calc)},B,N_{P=0}}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}} - \frac{2\left(\frac{\partial^2 F}{\partial C \partial P_{r(calc)}}\right)^o_{r,B,N_{P=0}} \left(\frac{\partial F}{\partial C}\right)^o_{r,P_{r(calc)},B,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\frac{\partial F}{\partial C}\right)^{o^2}_{r,P_{r(calc)},B,N_{P=0}} \left(\frac{\partial^2 F}{\partial P^2_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^3} \right] \tag{46}$$

$$\left(\frac{\partial^2 Y_r}{\partial B \partial N_{P=0}}\right)^o_{r,P_{r(obs)},C} = \left[\frac{\left(\frac{\partial^2 F}{\partial N_{P=0}\partial B}\right)^o_{r,P_{r(calc)},C}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}} - \frac{\left(\frac{\partial^2 F}{\partial B \partial P_{r(calc)}}\right)^o_{r,C,N_{P=0}} \left(\frac{\partial F}{\partial N_{P=0}}\right)^o_{r,P_{r(calc)},B,C}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} - \frac{\left(\frac{\partial F}{\partial B}\right)^o_{r,P_{r(calc)},C,N_{P=0}} \left(\frac{\partial^2 F}{\partial P_{r(calc)}\partial N_{P=0}}\right)^o_{r,B,C}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\frac{\partial F}{\partial B}\right)^o_{r,P_{r(calc)},C,N_{P=0}} \left(\frac{\partial F}{\partial N_{P=0}}\right)^o_{r,P_{r(calc)},B,C} \left(\frac{\partial^2 F}{\partial P^2_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^3} \right] \tag{47}$$

$$\left(\frac{\partial^2 Y_r}{\partial C \partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},B} = \left[\frac{\left(\frac{\partial^2 F}{\partial N_{P=0} \partial C}\right)^{o}_{r,P_{r(calc)},B}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^{o}_{r,B,C,N_{P=0}}} - \frac{\left(\frac{\partial^2 F}{\partial C \partial P_{r(calc)}}\right)^{o}_{r,B,N_{P=0}} \left(\frac{\partial F}{\partial N_{P=0}}\right)^{o}_{r,P_{r(calc)},B,C}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^{o}_{r,B,C,N_{P=0}}\right]^2} - \frac{\left(\frac{\partial F}{\partial C}\right)^{o}_{r,P_{r(calc)},B,N_{P=0}} \left(\frac{\partial^2 F}{\partial P_{r(calc)} \partial N_{P=0}}\right)^{o}_{r,B,C}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^{o}_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\frac{\partial F}{\partial C}\right)^{o}_{r,P_{r(calc)},B,N_{P=0}} \left(\frac{\partial F}{\partial N_{P=0}}\right)^{o}_{r,P_{r(calc)},B,C} \left(\frac{\partial^2 F}{\partial P^2_{r(calc)}}\right)^{o}_{r,B,C,N_{P=0}}}{\left[\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^{o}_{r,B,C,N_{P=0}}\right]^3} \right] \tag{48}$$

$$\left(\frac{\partial^2 Y_r}{\partial N_{P=0}^2}\right)^o_{r,P_{r(obs)},B,C} = \left[\frac{\left(\dfrac{\partial^2 F}{\partial N_{P=0}^2}\right)^o_{r,P_{r(calc)},B,C}}{\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}} - \frac{2\left(\dfrac{\partial^2 F}{\partial N_{P=0}\partial P_{r(calc)}}\right)^o_{r,B,C}\left(\dfrac{\partial F}{\partial N_{P=0}}\right)^o_{r,P_{r(calc)},B,C}}{\left[\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\dfrac{\partial F}{\partial N_{P=0}}\right)^{o\,2}_{r,P_{r(calc)},B,C}\left(\dfrac{\partial^2 F}{\partial P_{r(calc)}^2}\right)^o_{r,B,C,N_{P=0}}}{\left[\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^3}\right] \tag{49}$$

$$\left(\frac{\partial^2 Y_r}{\partial B\partial C}\right)^o_{r,P_{r(obs)},N_{P=0}} = \left[\frac{\left(\dfrac{\partial^2 F}{\partial C\partial B}\right)^o_{r,P_{r(calc)},N_{P=0}}}{\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}} - \frac{\left(\dfrac{\partial^2 F}{\partial B\partial P_{r(calc)}}\right)^o_{r,C,N_{P=0}}\left(\dfrac{\partial F}{\partial C}\right)^o_{r,P_{r(calc)},B,N_{P=0}}}{\left[\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} - \frac{\left(\dfrac{\partial F}{\partial B}\right)^o_{r,P_{r(calc)},C,N_{P=0}}\left(\dfrac{\partial^2 F}{\partial P_{r(calc)}\partial C}\right)^o_{r,B,N_{P=0}}}{\left[\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^2} + \frac{\left(\dfrac{\partial F}{\partial B}\right)^o_{r,P_{r(calc)},C,N_{P=0}}\left(\dfrac{\partial F}{\partial C}\right)_{r,P_{r(calc)},B,N_{P=0}}\left(\dfrac{\partial^2 F}{\partial P_{r(calc)}^2}\right)^o_{r,B,C,N_{P=0}}}{\left[\left(\dfrac{\partial F}{\partial P_{r(calc)}}\right)^o_{r,B,C,N_{P=0}}\right]^3}\right] \tag{50}$$

$$Y_r^o = [P_{r(obs)} - P_{r(calc)}]^o \tag{23}$$

Now in order to evaluate the constants of the linearized normal equations, we need values of first and second derivatives of the function, F,

$$F = F(r, P_{r(calc)}, N_{P=0}, B, C) = 0 \tag{19}$$

By differentiating equation (19), we find that these derivatives are

$$\left(\frac{\partial F}{\partial B}\right)_{r,P_r,N_{P=0},C} = \left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} - \frac{N_{P=0}^r}{P_o} f_r P_r \left(\frac{\partial Z_o}{\partial B}\right)_{P_o,C} \tag{51}$$

$$\left(\frac{\partial F}{\partial C}\right)_{r,P_r,N_{P=0},B} = \left(\frac{\partial Z_r}{\partial C}\right)_{P_r,B} - \frac{N_{P=0}^r}{P_o} f_r P_r \left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} \tag{52}$$

$$\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,P_r,B,C} = -\frac{rZ_o}{P_o} N_{P=0}^{r-1} f_r P_r \tag{53}$$

$$\left(\frac{\partial F}{\partial P_r}\right)_{r,N_{P=0},B,C} = \left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} - \frac{Z_o}{P_o} N_{P=0}^r f_r - \frac{Z_o}{P_o} N_{P=0}^r P_r \left(\frac{\partial f_r}{\partial P_r}\right) \tag{54}$$

But,

$$\left(\frac{\partial f_r}{\partial P_r}\right) = \frac{f_r \alpha}{1 + \alpha P_r} \tag{55}$$

Therefore, substituting equation (55) in equation (54),

$$\left(\frac{\partial F}{\partial P_r}\right)_{r,N_{P=0},B,C} = \left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} - \frac{Z_o}{P_o} N_{P=0}^r f_r \left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right) \tag{56}$$

$$\left(\frac{\partial^2 F}{\partial B^2}\right)_{r,P_r,N_{P=0},C} = \left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{P_r,C} - \frac{N_{P=0}^r}{P_o} f_r P_r \left(\frac{\partial^2 Z_o}{\partial B^2}\right)_{P_o,C} \quad (57)$$

$$\left(\frac{\partial^2 F}{\partial C^2}\right)_{r,P_r,N_{P=0},B} = \left(\frac{\partial^2 Z_r}{\partial C^2}\right)_{P_r,B} - \frac{N_{P=0}^r}{P_o} f_r P_r \left(\frac{\partial^2 Z_o}{\partial C^2}\right)_{P_o,B} \quad (58)$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0}^2}\right)_{r,P_r,B,C} = \frac{-r(r-1)Z_o}{P_o} N_{P=0}^{r-2} f_r P_r \quad (59)$$

$$\left(\frac{\partial^2 F}{\partial P_r^2}\right)_{r,N_{P=0},B,C} = \left(\frac{\partial^2 Z_r}{\partial P_r^2}\right)_{B,C} - \frac{2Z_o}{P_o} N_{P=0}^r \left(\frac{\partial f_r}{\partial P_r}\right) - \frac{Z_o}{P_o} N_{P=0}^r P_r \left(\frac{\partial^2 f_r}{\partial P_r^2}\right) \quad (60)$$

$$\left(\frac{\partial f_r}{\partial P_r}\right) = \frac{f_r \alpha}{1+\alpha P_r} \quad (55)$$

$$\frac{\partial^2 f_r}{\partial P_r^2} = \frac{\alpha}{1+\alpha P_r}\left(\frac{\partial f_r}{\partial P_r}\right) - \frac{f_r \alpha^2}{(1+\alpha P_r)^2}$$

$$\frac{\partial^2 f_r}{\partial P_r^2} = \frac{f_r \alpha^2}{(1+\alpha P_r)^2} - \frac{f_r \alpha^2}{(1+\alpha P_r)^2} = 0 \quad (61)$$

Therefore,

$$\left(\frac{\partial^2 F}{\partial P_r^2}\right)_{r,N_{P=0},B,C} = \left(\frac{\partial^2 Z_r}{\partial P_r^2}\right)_{B,C} - \frac{2Z_o}{P_o} N_{P=0}^r \frac{f_r \alpha}{1+\alpha P_r} \quad (62)$$

$$\left(\frac{\partial^2 F}{\partial B \partial C}\right)_{r,P_r,N_{P=0}} = \left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{P_r} - \frac{N_{P=0}^r}{P_o} f_r P_r \left(\frac{\partial^2 Z_o}{\partial B \partial C}\right)_{P_o} \quad (63)$$

$$\left(\frac{\partial^2 F}{\partial B \partial N_{P=0}}\right)_{r,P_r,C} = \frac{-rN_{P=0}^{r-1} f_r P_r}{P_o} \left(\frac{\partial Z_o}{\partial B}\right)_{P_o,C} \tag{64}$$

$$\left(\frac{\partial^2 F}{\partial B \partial P_r}\right)_{r,N_{P=0},C} = \left(\frac{\partial^2 Z_r}{\partial B \partial P_r}\right)_C - \frac{N_{P=0}^{r} f_r}{P_o} \left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right)\left(\frac{\partial Z_o}{\partial B}\right)_{P_o,C} \tag{65}$$

$$\left(\frac{\partial^2 F}{\partial C \partial N_{P=0}}\right)_{r,P_r,B} = \frac{-rN_{P=0}^{r-1} f_r P_r}{P_o} \left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} \tag{66}$$

$$\left(\frac{\partial^2 F}{\partial C \partial P_r}\right)_{r,N_{P=0},B} = \left(\frac{\partial^2 Z_r}{\partial C \partial P_r}\right)_B - \frac{N_{P=0}^{r} f_r}{P_o} \left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right)\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} \tag{67}$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0} \partial P_r}\right)_{r,B,C} = \frac{-rZ_o N_{P=0}^{r-1} f_r}{P_o} \left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right) \tag{68}$$

The derivatives of F, as given by equations (51) - (68), are to be evaluated for $P_r = P_{r(calc)}$.

Now if Z_r is an explicit function of the pressure, P_r, then equations (51) - (68) can be used directly to calculate the various derivatives of the function, F. However, if Z_r is an explicit function of the molal density, ρ_r, then it is necessary to express the various derivatives of Z appearing in equations (51) - (68) as a function of the density, ρ_r.

We then have

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C} + \left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial \rho_r}{\partial B}\right)_{P_r,C} \tag{69}$$

Now

$$\rho_r = \frac{P_r}{RTZ_r} \tag{17}$$

Similarly,

$$\rho_o = \frac{P_o}{RTZ_o} \tag{70}$$

Differentiating equation (17) with regard to B, keeping P_r and C fixed, we have

$$\left(\frac{\partial \rho_r}{\partial B}\right)_{P_r,C} = \frac{-P_r}{RTZ_r^2}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} \tag{71}$$

and substituting equation (17) in equation (71)

$$\left(\frac{\partial \rho_r}{\partial B}\right)_{P_r,C} = \frac{-\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} \tag{72}$$

Then substituting equation (72) into equation (69), we have

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C} - \left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} \tag{73}$$

or, rearranging the above equation,

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{74}$$

Similarly,

$$\left(\frac{\partial Z_o}{\partial B}\right)_{P_o,C} = \frac{\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}}{1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} \tag{75}$$

Substituting equations (74) and (75) into equation (51), we have

$$\left(\frac{\partial F}{\partial B}\right)_{r,P_r,N_{P=0},C} = \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{N^r_{P=0} f_r P_r}{P_o} \frac{\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}}{1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} \tag{76}$$

$\left(\frac{\partial Z_r}{\partial C}\right)_{P_r,B}$ and $\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B}$ are of the same form as equations (74) and (75) and upon substituting these expressions into equation (52), we get an equation similar to equation (76) of the form

$$\left(\frac{\partial F}{\partial C}\right)_{P_r,B} = \frac{\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{N^r_{P=0} f_r P_r}{P_o} \frac{\left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}}{1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} \tag{77}$$

Since Z_r and Z_o are functions of the parameters B and C but not of $N_{P=0}$, then

$$\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,P_r,B,C} = \frac{-r\ Z_o\ N^{r-1}_{P=0}\ f_r P_r}{P_o} \tag{53}$$

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = \left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} \tag{78}$$

Differentiating equation (17) with regard to P_r, keeping B and C fixed, we have

$$\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} = \frac{1}{RTZ_r} - \frac{P_r}{RTZ_r^2}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} \tag{79}$$

or, substituting equation (17) into equation (79),

$$\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} = \frac{\rho_r}{P_r} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} \tag{80}$$

Substituting equation (80) into equation (78), we have

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = \frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} \tag{81}$$

or,

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{82}$$

Substituting equation (82) into equation (56), we have

$$\left(\frac{\partial F}{\partial P_r}\right)_{r,N_{P=0},B,C} = \frac{\rho_r\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{P_r\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]} - \frac{Z_o}{P_o} N^r_{P=0}\, f_r\left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right) \tag{83}$$

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \text{function}(\rho_r, B, C) \tag{84}$$

$$d\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C} d\rho_r + \left[\frac{\partial}{\partial B}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,C} dB + \left[\frac{\partial}{\partial C}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,B} dC \tag{85}$$

$$\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{P_r,C} = \left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C}\left(\frac{\partial \rho_r}{\partial B}\right)_{P_r,C} + \left[\frac{\partial}{\partial B}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,C} \tag{86}$$

But from equation (74), we have

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{74}$$

Differentiating equation (74) with regard to B keeping ρ_r and C fixed,

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,C} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial B \partial \rho_r}\right)_C - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2}\right] \tag{87}$$

$$\left[\frac{\partial}{\partial B}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,C} = \left[\begin{array}{l} \dfrac{\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{\rho_r,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{\rho_r,C}}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} \\ + \dfrac{\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial B}\right)^2_{\rho_r,C} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial^2 Z_r}{\partial B \partial \rho_r}\right)_C}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} \end{array}\right] \tag{88}$$

$$\left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial B \partial \rho_r}\right)_C}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)^2_{B,C}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2}\right] \tag{89}$$

$$\left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial B \partial \rho_r}\right)_C + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial^2 Z_r}{\partial B \partial \rho_r}\right)_C}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} + \frac{\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial Z_r}{\partial \rho_r}\right)^2_{B,C} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2}\right] \tag{90}$$

$$\left(\frac{\partial \rho_r}{\partial B}\right)_{P_r,C} = -\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} \tag{72}$$

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{74}$$

Substituting equation (74) into equation (72), we have

$$\left(\frac{\partial\rho_r}{\partial B}\right)_{P_r,C} = -\frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}} \tag{91}$$

Multiplying equation (91) by equation (90), we have

$$\left[\frac{\partial}{\partial\rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C}\left(\frac{\partial\rho_r}{\partial B}\right)_{P_r,C} = \left[\frac{-\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial^2 Z_r}{\partial B\partial\rho_r}\right)_C}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^2} + \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)^2_{\rho_r,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}+\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial\rho_r^2}\right)_{B,C}-\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial\rho_r}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^3}\right] \tag{92}$$

Substituting equations (88) and (92) into equation (86), we have

$$\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{P_r,C} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{\rho_r,C}}{1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}} - \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[2\left(\frac{\partial^2 Z_r}{\partial B\partial\rho_r}\right)_C-\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^2} + \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)^2_{\rho_r,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}+\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial\rho_r^2}\right)_{B,C}-\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial\rho_r}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^3}\right] \tag{93}$$

Similarly,

$$\left(\frac{\partial^2 Z_o}{\partial B^2}\right)_{P_o,C} = \left[\frac{\left(\frac{\partial^2 Z_o}{\partial B^2}\right)_{\rho_o,C}}{1+\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} - \frac{\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}\left[2\left(\frac{\partial^2 Z_o}{\partial B\partial\rho_o}\right)_C - \frac{1}{Z_o}\left(\frac{\partial Z_o}{\partial\rho_o}\right)_{B,C}\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}\right]}{\left[1+\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial\rho_o}\right)_{B,C}\right]^2} + \frac{\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial B}\right)^2_{\rho_o,C}\left[\frac{1}{Z_o}\left(\frac{\partial Z_o}{\partial\rho_o}\right)_{B,C} + \frac{\rho_o}{Z_o}\left(\frac{\partial^2 Z_o}{\partial\rho_o^2}\right)_{B,C} - \frac{\rho_o}{Z_o^2}\left(\frac{\partial Z_o}{\partial\rho_o}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial\rho_o}\right)_{B,C}\right]^3}\right] \tag{94}$$

Equations (93) and (94) are to be used in equation (57).

The $\left(\frac{\partial^2 Z_r}{\partial C^2}\right)_{P_r,B}$ and the $\left(\frac{\partial^2 Z_o}{\partial C^2}\right)_{P_o,B}$ are obtained in the same manner as equations (93) and (94) and are of the form

$$\left(\frac{\partial^2 Z_r}{\partial C^2}\right)_{P_r,B} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial C^2}\right)_{\rho_r,B}}{1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left[2\left(\frac{\partial^2 Z_r}{\partial C\partial\rho_r}\right)_B - \frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^2} + \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial C}\right)^2_{\rho_r,B}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial\rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial\rho_r}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^3}\right] \tag{95}$$

$$\left(\frac{\partial^2 Z_o}{\partial C^2}\right)_{P_o,B} = \left[\frac{\left(\frac{\partial^2 Z_o}{\partial C^2}\right)_{\rho_o,B}}{1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} - \frac{\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}\left[2\left(\frac{\partial^2 Z_o}{\partial C \partial \rho_o}\right)_B - \frac{1}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}\right]}{\left[1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]^2} + \frac{\frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial C}\right)^2_{\rho_o,B}\left[\frac{1}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C} + \frac{\rho_o}{Z_o}\left(\frac{\partial^2 Z_o}{\partial \rho_o^2}\right)_{B,C} - \frac{\rho_o}{Z_o^2}\left(\frac{\partial Z_o}{\partial \rho_o}\right)^2_{B,C}\right]}{\left[1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]^3} \right] \tag{96}$$

Equations (95) and (96) are to be substituted in equation (58).

$$\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,P_r,B,C} = \frac{-rZ_o N_{P=0}^{r-1} f_r P_r}{P_o} \tag{53}$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0}^2}\right)_{r,P_r,B,C} = \frac{-r(r-1)Z_o N_{P=0}^{r-2} f_r P_r}{P_o} \tag{59}$$

From equation (82), we have

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{82}$$

and differentiating the above expression with respect to P_r, keeping B and C fixed,

$$\left(\frac{\partial^2 Z_r}{\partial P_r^2}\right)_{B,C} = \left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C}\right]_{B,C}\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} \tag{97}$$

Differentiating equation (82) with regard to ρ_r, keeping B and C fixed, we have

$$\left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C}\right]_{B,C} = \left[\frac{\frac{1}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{P_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{P_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial P_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}^2\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2}\right] \tag{98}$$

$$\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} = \frac{\rho_r}{P_r} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} \tag{80}$$

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{82}$$

Substituting equation (82) into equation (80), we have

$$\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} = \frac{\rho_r}{P_r}\left[1 - \frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}\right] \tag{99}$$

or

$$\left(\frac{\partial \rho_r}{\partial P_r}\right)_{B,C} = \frac{\frac{\rho_r}{P_r}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \tag{100}$$

Multiplying equation (98) by equation (100) and substituting into equation (97), we have

$$\left(\frac{\partial^2 Z_r}{\partial P_r^2}\right)_{B,C} = \left[- \frac{\frac{\rho_r}{P_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} + \frac{\frac{\rho_r}{P_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r^2}{P_r^2}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C}}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} - \frac{\frac{\rho_r^2}{P_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}^2\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^3} \right] \quad (101)$$

Equation (101) is to be substituted in equation (62).

Differentiating equation (85) with regard to C, keeping P_r and B fixed, we get

$$\left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{P_r} = \left[\frac{\partial}{\partial \rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C}\left(\frac{\partial \rho_r}{\partial C}\right)_{P_r,B} + \left[\frac{\partial}{\partial C}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,B} \quad (102)$$

From equation (74), we have

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} \quad (74)$$

Differentiating the above expression with regard to first C, keeping ρ_r and B fixed, and then with regard to ρ_r, keeping B and C fixed, we get

$$\left[\frac{\partial}{\partial C}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{\rho_r,B} = \frac{\left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{\rho_r}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r \partial C}\right)_B - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} \quad (103)$$

and

$$\left[\frac{\partial}{\partial\rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C} = \frac{\left(\frac{\partial^2 Z_r}{\partial\rho_r\partial B}\right)_C}{1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}} - \frac{\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}+\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial\rho_r^2}\right)_{B,C}-\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial\rho_r}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^2} \tag{104}$$

As for equation (91), it can be shown that

$$\left(\frac{\partial\rho_r}{\partial C}\right)_{P_r,B} = -\frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}}{1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}} \tag{105}$$

Multiplying equations (104) and (105), we have

$$\left[\frac{\partial}{\partial\rho_r}\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C}\right]_{B,C}\left(\frac{\partial\rho_r}{\partial C}\right)_{P_r,B} = -\frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left(\frac{\partial^2 Z_r}{\partial\rho_r\partial B}\right)_C}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^2}$$
$$+\frac{\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}+\frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial\rho_r^2}\right)_{B,C}-\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial\rho_r}\right)^2_{B,C}\right]}{\left[1+\frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial\rho_r}\right)_{B,C}\right]^3} \tag{106}$$

Adding equations (103) and (106), and then substituting into equation (102), we have

$$\left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{P_r} = \left[\frac{\left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{\rho_r}}{1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}} - \frac{\frac{\rho_r}{Z_r}\left[\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial^2 Z_r}{\partial \rho_r \partial C}\right)_B + \left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left(\frac{\partial^2 Z_r}{\partial \rho_r \partial B}\right)_C - \frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} + \frac{\frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left[\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \rho_r\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}^2\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^3} \right] \quad (107)$$

Similarly,

$$\left(\frac{\partial^2 Z_o}{\partial B \partial C}\right)_{P_o} = \left[\frac{\left(\frac{\partial^2 Z_o}{\partial B \partial C}\right)_{\rho_o}}{1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} - \frac{\frac{\rho_o}{Z_o}\left[\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}\left(\frac{\partial^2 Z_o}{\partial \rho_o \partial C}\right)_B + \left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}\left(\frac{\partial^2 Z_o}{\partial \rho_o \partial B}\right)_C - \frac{1}{Z_o}\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}\left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]}{\left[1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]^2} + \frac{\frac{\rho_o}{Z_o^2}\left(\frac{\partial Z_o}{\partial B}\right)_{\rho_o,C}\left(\frac{\partial Z_o}{\partial C}\right)_{\rho_o,B}\left[\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C} + \rho_o\left(\frac{\partial^2 Z_o}{\partial \rho_o^2}\right)_{B,C} - \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}^2\right]}{\left[1 + \frac{\rho_o}{Z_o}\left(\frac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]^3} \right] \quad (108)$$

May 12, 1966

Memorandum

To: L. W. Brandt
H. P. Wheeler (2)
Project Control Office (2)
R. E. Barieau (2)
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From: B. J. Dalton and Robert E. Barieau

Subject: Addendum to Helium Research Center Internal Report No. 86, "Method for Treating PVT Data from a Burnett Compressibility Apparatus," by Robert E. Barieau and B. J. Dalton

Page 35, equation (111) should be

$$\left(\frac{\partial^2 Z_r}{\partial P_r \partial B}\right)_C = \left[\frac{\frac{\rho_r}{P_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r \partial B}\right)_C}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} - \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)^2_{B,C}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^3} \right] \qquad (111)$$

B. J. Dalton

Robert E. Barieau

$$\left(\frac{\partial^2 Z_r}{\partial P_r \partial B}\right)_C = \left[\begin{array}{c} \dfrac{\dfrac{\rho_r}{P_r}\left(\dfrac{\partial^2 Z_r}{\partial \rho_r \partial B}\right)_C}{\left[1 + \dfrac{\rho_r}{Z_r}\left(\dfrac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} \\ \\ \dfrac{- \dfrac{\rho_r}{P_r}\left(\dfrac{\partial Z_r}{\partial B}\right)_{\rho_r,C}\left[\dfrac{1}{Z_r}\left(\dfrac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \dfrac{\rho_r}{Z_r}\left(\dfrac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \dfrac{\rho_r}{Z_r^2}\left(\dfrac{\partial Z_r}{\partial \rho_r}\right)^2_{B,C}\right]}{\left[1 + \dfrac{\rho_r}{Z_r}\left(\dfrac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^3} \end{array} \right] \tag{111}$$

Equations (75) and (111) are to be substituted into equation (65).

$$\left(\frac{\partial^2 F}{\partial C \partial N_{P=0}}\right)_{r,P_r,B} = \frac{-rN^{r-1}_{P=0}\, f_r P_r}{P_o}\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} \tag{66}$$

$$\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} = \frac{\left(\dfrac{\partial Z_o}{\partial C}\right)_{\rho_o,B}}{1 + \dfrac{\rho_o}{Z_o}\left(\dfrac{\partial Z_o}{\partial \rho_o}\right)_{B,C}} \tag{112}$$

Substituting equation (112) into equation (66), we get

$$\left(\frac{\partial^2 F}{\partial C \partial N_{P=0}}\right)_{r,P_r,B} = - \frac{rN^{r-1}_{P=0}\, f_r P_r \left(\dfrac{\partial Z_o}{\partial C}\right)_{\rho_o,B}}{P_o\left[1 + \dfrac{\rho_o}{Z_o}\left(\dfrac{\partial Z_o}{\partial \rho_o}\right)_{B,C}\right]} \tag{113}$$

From equation (67), we have

$$\left(\frac{\partial^2 F}{\partial C \partial P_r}\right)_{r,B} = \left(\frac{\partial^2 Z_r}{\partial C \partial P_r}\right)_B - \frac{N^r_{P=0}\ f_r}{P_o}\left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right)\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} \quad (67)$$

Now the first term on the right-hand side of the above equation is obtained in the same manner as $\left(\frac{\partial^2 Z_r}{\partial P_r \partial B}\right)_C$ of equation (111) and is of the form

$$\left(\frac{\partial^2 Z_r}{\partial C \partial P_r}\right)_B = \frac{\frac{\rho_r}{P_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r \partial C}\right)_B}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^2} - \frac{\frac{\rho_r}{P_r}\left(\frac{\partial Z_r}{\partial C}\right)_{\rho_r,B}\left[\frac{1}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C} + \frac{\rho_r}{Z_r}\left(\frac{\partial^2 Z_r}{\partial \rho_r^2}\right)_{B,C} - \frac{\rho_r}{Z_r^2}\left(\frac{\partial Z_r}{\partial \rho_r}\right)^2_{B,C}\right]}{\left[1 + \frac{\rho_r}{Z_r}\left(\frac{\partial Z_r}{\partial \rho_r}\right)_{B,C}\right]^3} \quad (114)$$

Equations (112) and (113) are to be substituted into equation (67).

$$\left(\frac{\partial^2 F}{\partial N_{P=0} \partial P_r}\right)_{r,B,C} = \frac{-rZ_o N^{r-1}_{P=0}\ f_r}{P_o}\left(1 + \frac{\alpha P_r}{1+\alpha P_r}\right) \quad (68)$$

We will now apply these formulas to the special case when the compressibility, Z, can be expressed as

$$Z_r = 1 + BP_r + CP_r^2 \quad (115)$$

This expression is linear in the constants B and C. However, the equations previously given apply to any functional form for B, C, ..., linear or non-linear.

We have by differentiating equation (114)

$$\left(\frac{\partial Z_r}{\partial B}\right)_{P_r,C} = P_r \quad (116)$$

$$\left(\frac{\partial Z_r}{\partial C}\right)_{P_r,B} = P_r^2 \tag{117}$$

$$\left(\frac{\partial Z_r}{\partial P_r}\right)_{B,C} = B + 2CP_r \tag{118}$$

$$\left(\frac{\partial^2 Z_r}{\partial B^2}\right)_{P_r,C} = 0 \tag{119}$$

$$\left(\frac{\partial^2 Z_r}{\partial C^2}\right)_{P_r,B} = 0 \tag{120}$$

$$\left(\frac{\partial^2 Z_r}{\partial P_r^2}\right)_{B,C} = 2C \tag{121}$$

$$\left(\frac{\partial^2 Z_r}{\partial B \partial C}\right)_{P_r} = 0 \tag{122}$$

$$\left(\frac{\partial^2 Z_r}{\partial B \partial P_r}\right)_{C} = 1 \tag{123}$$

$$\left(\frac{\partial^2 Z_r}{\partial C \partial P_r}\right)_{B} = 2P_r \tag{124}$$

Also,

$$Z_o = 1 + BP_o + CP_o^2 \tag{125}$$

so that

$$\left(\frac{\partial Z_o}{\partial B}\right)_{P_o,C} = P_o \tag{126}$$

$$\left(\frac{\partial Z_o}{\partial C}\right)_{P_o,B} = P_o^2 \qquad (127)$$

$$\left(\frac{\partial^2 Z_o}{\partial B^2}\right)_{P_o,C} = 0 \qquad (128)$$

$$\left(\frac{\partial^2 Z_o}{\partial C^2}\right)_{P_o,B} = 0 \qquad (129)$$

$$\left(\frac{\partial^2 Z_o}{\partial B \partial C}\right)_{P_o} = 0 \qquad (130)$$

Substituting equations (116) - (130) into equations (51) - (68), we find

$$\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}} = P_{r(calc)}(1 - f_{r(calc)}N_{P=0}^{r}) \qquad (131)$$

$$\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}} = P_{r(calc)}\left[P_{r(calc)} - f_{r(calc)}N_{P=0}^{r}P_o\right] \qquad (132)$$

$$\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}} = -r(Z_o/P_o)f_{r(calc)}N_{P=0}^{r-1}\,P_{r(calc)} \qquad (133)$$

$$\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{r,B,C,N_{P=0}} = B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N_{P=0}^{r}\left[1 + \frac{\alpha P_{r(calc)}}{(1 + \alpha P_{r(calc)})}\right] \qquad (134)$$

$$\left(\frac{\partial^2 F}{\partial B^2}\right)_{r,C,N_{P=0},P_{r(calc)}} = 0 \qquad (135)$$

$$\left(\frac{\partial^2 F}{\partial C^2}\right)_{r,B,N_{P=0},P_{r(calc)}} = 0 \qquad (136)$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0}^2}\right)_{r,B,C,P_{r(calc)}} = -r(r-1)\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-2}\, P_{r(calc)} \qquad (137)$$

$$\left(\frac{\partial^2 F}{\partial P_{r(calc)}^2}\right)_{r,B,C,N_{P=0}} = 2C - 2\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(\frac{\alpha}{1+\alpha P_{r(calc)}}\right) \qquad (138)$$

$$\left(\frac{\partial^2 F}{\partial B \partial C}\right)_{r,N_{P=0},P_{r(calc)}} = 0 \qquad (139)$$

$$\left(\frac{\partial^2 F}{\partial B \partial N_{P=0}}\right)_{r,C,P_{r(calc)}} = -r f_{r(calc)} N_{P=0}^{r-1}\, P_{r(calc)} \qquad (140)$$

$$\left(\frac{\partial^2 F}{\partial B \partial P_{r(calc)}}\right)_{r,C,N_{P=0}} = 1 - f_{r(calc)} N_{P=0}^{r}\left[1 + \frac{\alpha P_{r(calc)}}{1+\alpha P_{r(calc)}}\right] \qquad (141)$$

$$\left(\frac{\partial^2 F}{\partial C \partial N_{P=0}}\right)_{r,B,P_{r(calc)}} = -r P_o f_{r(calc)} N_{P=0}^{r-1}\, P_{r(calc)} \qquad (142)$$

$$\left(\frac{\partial^2 F}{\partial C \partial P_{r(calc)}}\right)_{r,B,N_{P=0}} = 2P_{r(calc)} - f_{r(calc)} N_{P=0}^{r}\, P_o\left[1 + \frac{\alpha P_{r(calc)}}{1+\alpha P_{r(calc)}}\right] \qquad (143)$$

$$\left(\frac{\partial^2 F}{\partial N_{P=0} \partial P_{r(calc)}}\right)_{r,B,C} = \frac{-r Z_o f_{r(calc)} N_{P=0}^{r-1}}{P_o}\left[1 + \frac{\alpha P_{r(calc)}}{1+\alpha P_{r(calc)}}\right] \qquad (144)$$

Substituting equations (131) - (144) into equations (42) - (50), we have

$$\left(\frac{\partial Y_r}{\partial B}\right)^o_{r,P_{r(obs)},C,N_{P=0}} = \frac{P_{r(calc)}\left[1 - f_{r(calc)}N^r_{P=0}\right]}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]} \tag{145}$$

$$\left(\frac{\partial Y_r}{\partial C}\right)^o_{r,P_{r(obs)},B,N_{P=0}} = \frac{P_{r(calc)}\left[P_{r(calc)} - f_{r(calc)}N^r_{P=0}\, P_o\right]}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]} \tag{146}$$

$$\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^o_{r,P_{r(obs)},B,C} = \frac{-r(Z_o/P_o)f_{r(calc)}N^{r-1}_{P=0}\, P_{r(calc)}}{B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]} \tag{147}$$

$$\left(\frac{\partial^2 Y_r}{\partial B^2}\right)^o_{r,P_{r(obs)},C,N_{P=0}} = \left[\begin{gathered}\frac{-2P_{r(calc)}\left(1 - f_{r(calc)}N^r_{P=0}\right)\left[1 - f_{r(calc)}N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]\right]^2} \\[2em] + \frac{2P^2_{r(calc)}\left(1 - f_{r(calc)}N^r_{P=0}\right)^2\left[C - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\frac{\alpha}{(1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^r_{P=0}\left[1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right]\right]^3}\end{gathered}\right] \tag{148}$$

$$\left(\frac{\partial^2 Y_r}{\partial C^2}\right)^{o}_{r,P_{r(obs)},B,N_{P=0}} = \left[\frac{-\,2P_{r(calc)}\left[P_{r(calc)} - f_{r(calc)}N^{r}_{P=0}\,P_o\right]\left[2P_{r(calc)} - f_{r(calc)}N^{r}_{P=0}\,P_o\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}\,N^{r}_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} + \frac{2P^2_{r(calc)}\left[P_{r(calc)} - f_{r(calc)}N^{r}_{P=0}\,P_o\right]^2\left[C - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^{r}_{P=0}\,\frac{\alpha}{(1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right)f_{r(calc)}N^{r}_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^3}\right] \qquad (149)$$

$$\left(\frac{\partial^2 Y_r}{\partial N_{P=0}^2}\right)^{o}_{r,P_{r(obs)},B,C} = \left[\frac{-\,r(r-1)\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-2}\, P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]} - \frac{2\left[r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\right]^2 P_{r(calc)}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} + \frac{2\left[r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\, P_{r(calc)}\right]^2\left[C - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\, \frac{\alpha}{(1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^3} \right] \quad (150)$$

$$\left(\frac{\partial^2 Y_r}{\partial B \partial C}\right)^o_{r, P_{r(obs)}, N_{P=0}} = \left[\frac{- P_{r(calc)}\left(P_{r(calc)} - f_{r(calc)} N^r_{P=0} P_o\right)\left[1 - f_{r(calc)} N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \right.$$

$$\frac{- P_{r(calc)}\left(1 - f_{r(calc)} N^r_{P=0}\right)\left[2P_{r(calc)} - f_{r(calc)} N^r_{P=0} P_o\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \tag{151}$$

$$\left. \frac{+ 2P^2_{r(calc)}\left(1 - f_{r(calc)} N^r_{P=0}\right)\left(P_{r(calc)} - f_{r(calc)} N^r_{P=0} P_o\right)\left[C - \frac{Z_o f_{r(calc)} N^r_{P=0}\, \alpha}{P_o (1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N^r_{P=0}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^3} \right]$$

$$\left(\frac{\partial^2 Y_r}{\partial B \partial N_{P=0}}\right)^{o}_{r,P_{r(obs)},C} = \left[\begin{array}{c}
\dfrac{- r\, f_{r(calc)} N_{P=0}^{r-1}\, P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]} \\[4ex]
+ \dfrac{r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\, P_{r(calc)} \left[1 - f_{r(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \\[4ex]
+ \dfrac{P_{r(calc)} \left(1 - f_{r(calc)} N_{P=0}^{r}\right) r \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \\[4ex]
- \dfrac{2P_{r(calc)}^{2} \left(1 - f_{r(calc)} N_{P=0}^{r}\right) r \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1} \left[C - \frac{Z_o f_{r(calc)} N_{P=0}^{r}\, \alpha}{P_o (1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r} \left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^3}
\end{array}\right] \tag{152}$$

$$
\left(\frac{\partial^2 Y_r}{\partial C\,\partial N_{P=0}}\right)^{o}_{r,\,P_{r(obs)},\,B} = \left[
\begin{aligned}
&\frac{-\,r\,P_o f_{r(calc)} N_{P=0}^{r-1}\,P_{r(calc)}}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]} \\[2ex]
&+\frac{r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\,P_{r(calc)}\left[2P_{r(calc)} - f_{r(calc)} N_{P=0}^{r} P_o\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \\[2ex]
&+\frac{P_{r(calc)}\left(P_{r(calc)} - f_{r(calc)} N_{P=0}^{r} P_o\right) r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^2} \\[2ex]
&-\frac{2P_{r(calc)}^{2}\left(P_{r(calc)} - f_{r(calc)} N_{P=0}^{r} P_o\right) r\left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r-1}\left[C - \frac{Z_o f_{r(calc)} N_{P=0}^{r}\,\alpha}{P_o(1+\alpha P_{r(calc)})}\right]}{\left[B + 2CP_{r(calc)} - \left(\frac{Z_o}{P_o}\right) f_{r(calc)} N_{P=0}^{r}\left(1 + \frac{\alpha P_{r(calc)}}{(1+\alpha P_{r(calc)})}\right)\right]^3}
\end{aligned}
\right] \qquad (153)
$$

The quantities given by equations (145) - (153) are to be substituted in equations (33) - (41), and then summed over all the observed pressures from P_1 to $P_r = P_n$. The initial pressure, P_o, is omitted from this sum because equation (18) is exactly satisfied for $P = P_o$. There is, therefore, no residual for the initial pressure, P_o.

The solutions to equations (29), (30), and (31) are:

$$D_o \Delta B = D_1 m_1 + D_2 m_2 + D_3 m_3 \tag{154}$$

$$D_o \Delta C = D_4 m_1 + D_5 m_2 + D_6 m_3 \tag{155}$$

$$D_o \Delta N_{P=0} = D_7 m_1 + D_8 m_2 + D_9 m_3 \tag{156}$$

where

$$D_1 = b_2 c_3 - b_3 c_2 \tag{157}$$

$$D_4 = D_2 = b_3 c_1 - b_1 c_3 \tag{158}$$

$$D_7 = D_3 = b_1 c_2 - b_2 c_1 \tag{159}$$

$$D_5 = a_1 c_3 - a_3 c_1 \tag{160}$$

$$D_8 = D_6 = a_2 c_1 - a_1 c_2 \tag{161}$$

$$D_9 = a_1 b_2 - a_2 b_1 \tag{162}$$

$$D_o = D_1 a_1 + D_2 a_2 + D_3 a_3 \tag{163}$$

If the assumed values for the undetermined constants were not too good, then it would be necessary to repeat the calculations using the new B, C, and $N_{P=0}$ as the start of a new iteration. We continue this iterative technique, provided the problem is continuing to converge, until $m_1 = m_2 = m_3 = 0$ to within some predetermined small quantity, the final B, C, and $N_{P=0}$ being the least squares solution for these constants. For a more detailed discussion of methods to use that will lead to convergence of the iteration when the problem starts diverging, we refer the reader to a previous report (1) on this subject.

EXPRESSIONS FOR CALCULATING VARIANCES AND COVARIANCES OF THE CONSTANTS EVALUATED

Once we have determined the best values for B, C, $N_{P=0}$, we proceed to calculate all variances and covariances of these constants. We do this from the definition of these quantities and the law for the propagation of errors (2, 4). This law states that if we have a function or quantity, say Q, that is a function of the independently-observed quantities y_1, y_2, ... , then the variance of the quantity Q is given as

$$S_Q^2 = \sum_{r=1}^{n} \left(\frac{\partial Q}{\partial y_{r(obs)}}\right)^2 S^2_{y_{r(obs)}} \tag{164}$$

where S_Q^2 is the variance of Q and $S^2_{y_{r(obs)}}$ is the variance of $y_{r(obs)}$. Extracting the square root of the variance, we obtain a value on the same scale as the function Q. This value, S_Q, is called the standard error or the standard deviation of Q.

The value of the constant B, which we have evaluated, is a function of all of the observed r's and of all of the observed P_r's. Since we have assumed the errors of the r's to be zero, then the expression for the variance of B is of the form

$$S_B^2 = \sum_{r=1}^{n} \left(\frac{\partial B}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \tag{165}$$

and there will be an equation similar to equation (165) for determining the variance of C and the variance of $N_{P=0}$.

In order to evaluate equation (165), we must evaluate $(\partial B/\partial P_{r(obs)})$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the product, and then sum the product over all of the observed P_r's.

In a previous report (1), we have outlined the details for evaluating the variances and covariances of the constants evaluated. For our particular problem, these variances and covariances are determined from the following relations:

$$S_B^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_1^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_2^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}} \\ & + D_3^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C} \\ & + 2D_1D_2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \\ & + 2D_1D_3 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \\ & + 2D_2D_3 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \end{aligned}\right] \quad (166)$$

$$S_C^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_4^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_5^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}} \\ & + D_6^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C} \\ & + 2D_4D_5 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \\ & + 2D_4D_6 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \\ & + 2D_5D_6 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \end{aligned}\right] \quad (167)$$

$$s^2_{N_{P=0}} = \frac{L^2}{D_o^2}\left[\begin{aligned}
&D_7^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_8^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}} \\
&+ D_9^2 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C} \\
&+ 2D_7D_8 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \\
&+ 2D_7D_9 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \\
&+ 2D_8D_9 \sum_{r=1}^{n} W_{P_{r(obs)}} \left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C}
\end{aligned}\right] \tag{168}$$

$$S_{BC}^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_1D_4\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_2D_5\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}} \\ & + D_3D_6\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C} \\ & + (D_2D_4 + D_1D_5)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \\ & + (D_1D_6 + D_3D_4)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \\ & + (D_2D_6 + D_3D_5)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \end{aligned}\right] \quad (169)$$

$$S_{BN_{P=0}}^2 = \frac{L^2}{D_o^2}\left[\begin{aligned} & D_1D_7\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_2D_8\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}} \\ & + D_3D_9\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C} \\ & + (D_1D_8 + D_2D_7)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}} \\ & + (D_1D_9 + D_3D_7)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \\ & + (D_2D_9 + D_3D_8)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C} \end{aligned}\right] \quad (170)$$

$$S^2_{CN_{P=0}} = \frac{L^2}{D_o^2}\left[\begin{aligned}&D_4D_7\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)^2_{r,P_{r(obs)},C,N_{P=0}} + D_5D_8\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)^2_{r,P_{r(obs)},B,N_{P=0}}\\ &+ D_6D_9\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)^2_{r,P_{r(obs)},B,C}\\ &+ (D_4D_8 + D_5D_7)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}}\\ &+ (D_4D_9 + D_6D_7)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial B}\right)_{r,P_{r(obs)},C,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C}\\ &+ (D_5D_9 + D_6D_8)\sum_{r=1}^{n} W_{P_{r(obs)}}\left(\frac{\partial Y_r}{\partial C}\right)_{r,P_{r(obs)},B,N_{P=0}}\left(\frac{\partial Y_r}{\partial N_{P=0}}\right)_{r,P_{r(obs)},B,C}\end{aligned}\right] \tag{171}$$

The remaining questions to be answered are: 1. what is the variance of the calculated P's and any other calculated P that reduces F to zero?; and 2. what is the variance of the compressibility factor?

EVALUATION OF THE VARIANCE OF THE $P_{r(calc)}$'S AND ANY OTHER CALCULATED P THAT REDUCES F TO ZERO

The variance of a calculated P_r which satisfies equation (19) for a given observed r value is obtained in the following way: $P_{r(calc)}$ is a function of the observed r's and, through the constants evaluated, is a function of all of the $P_{r(obs)}$'s. We see from equation (164) that the expression for determining the variance of $P_{r(calc)}$ involves evaluation of the quantity

$$S^2_{P_{r(calc)}} = \sum_{r=1}^{n} \left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \tag{172}$$

In order to evaluate the variance of the calculated P_r's, we need an expression for $[\partial P_{r(calc)}/\partial P_{r(obs)}]$. This quantity can be determined from equation (19)

$$F = F(r, P_{r(calc)}, N_{P=0}, B, C) \equiv 0 \tag{19}$$

We differentiate equation (19) with regard to $P_{r(obs)}$, holding r constant. This gives us

$$\left[\begin{array}{l}\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial B}\right)_{C,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right)\\ +\left(\frac{\partial F}{\partial C}\right)_{B,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right)+\left(\frac{\partial F}{\partial N_{P=0}}\right)_{B,C,r,P_{r(calc)}}\left(\frac{\partial N_{P=0}}{\partial P_{r(obs)}}\right)\end{array}\right] = 0 \quad (173)$$

Solving equation (173) for $[\partial P_{r(calc)}/\partial P_{r(obs)}]$, we get

$$\left(\frac{\partial P_{r(calc)}}{\partial P_{r(obs)}}\right) = -\left[\begin{array}{l}\dfrac{\left(\frac{\partial F}{\partial B}\right)_{C,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial B}{\partial P_{r(obs)}}\right)}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}}\\ +\dfrac{\left(\frac{\partial F}{\partial C}\right)_{B,r,N_{P=0},P_{r(calc)}}\left(\frac{\partial C}{\partial P_{r(obs)}}\right)}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}}\\ +\dfrac{\left(\frac{\partial F}{\partial N_{P=0}}\right)_{B,C,r,P_{r(calc)}}\left(\frac{\partial N_{P=0}}{\partial P_{r(obs)}}\right)}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)_{B,C,r,N_{P=0}}}\end{array}\right] \quad (174)$$

Multiplying equation (174) by $S_{P_{r(obs)}}$, squaring the product, and then summing over all of the observed P_r's, we get

$$s^2_{P_{r(calc)}} = \left[\frac{s^2_B \left(\frac{\partial F}{\partial B}\right)^2_{r,C,N_{P=0},P_{r(calc)}} + s^2_C \left(\frac{\partial F}{\partial C}\right)^2_{r,B,N_{P=0},P_{r(calc)}}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}} \right.$$

$$+ \frac{s^2_{N_{P=0}} \left(\frac{\partial F}{\partial N_{P=0}}\right)^2_{r,B,C,P_{r(calc)}}}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}}$$

$$+ \frac{2s^2_{BC}\left[\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}} \left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}}\right]}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}} \tag{175}$$

$$+ \frac{2s^2_{BN_{P=0}}\left[\left(\frac{\partial F}{\partial B}\right)_{r,C,N_{P=0},P_{r(calc)}} \left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}}$$

$$\left. + \frac{2s^2_{CN_{P=0}}\left[\left(\frac{\partial F}{\partial C}\right)_{r,B,N_{P=0},P_{r(calc)}} \left(\frac{\partial F}{\partial N_{P=0}}\right)_{r,B,C,P_{r(calc)}}\right]}{\left(\frac{\partial F}{\partial P_{r(calc)}}\right)^2_{r,B,C,N_{P=0}}} \right]$$

from which we can evaluate the values of $S^2_{P_{r(calc)}}$ corresponding to the observed r's.

Now we ask ourselves the question: how do we calculate the variance of any other calculated P that exactly satisfies equation (19)? In order to answer this question, we must find a value of r, say r_P, and we must find a value of f, evaluated at $P_{(calc)}$, which exactly satisfy the equation

$$Z_{P_{(calc)}} \equiv (Z_o/P_o) f_{(calc)}{}^{r_P} N_{P=0}\ P_{(calc)} \tag{176}$$

where

$$Z_{P_{(calc)}} = 1 + BP_{(calc)} + CP^2_{(calc)} \tag{177}$$

We have previously evaluated B, C, and $N_{P=0}$. We now proceed to evaluate f, which will be needed in equation (176). We do this as follows: from equation (15), $f_{(calc)}$ is of the form

$$f_{(calc)} = \frac{(1 + \alpha P_{1(calc)})(1 + \alpha P_{2(calc)}) \ldots (1 + \alpha P_{r(calc)})}{(1 + \beta P_o)(1 + \beta P_{1(calc)}) \ldots (1 + \beta P_{r-1(calc)})} \tag{178}$$

Our experimental determination of α and β, which appear in equation (15), indicates that α and β differ by less than 0.1 percent. In this section only, we therefore take $\alpha = \beta$. Then equation (178) can be written as

$$f_{(calc)} = \frac{(1 + \alpha P_{r(calc)})}{(1 + \alpha P_o)} \tag{179}$$

Experimentally, equations (176) and (179) apply only to integral values of r_P. However, in calculating the variance of $Z_{P(calc)}$ and of $P_{(calc)}$, we assume that equations (176) and (179) will apply to <u>any</u> value of the expansion number, r_P.

We are interested in calculating Z at even values of the pressure. We therefore calculate expansion numbers that will satisfy equation (176) for these even values of the pressure.

Now r_P, the expansion number corresponding to $P_{(calc)}$ and f evaluated at $P_{(calc)}$, can be determined from the equation

$$r_P = \left[\frac{\ln Z_{P(calc)} - \ln(Z_o/P_o) - \ln P_{(calc)} - \ln f_{(calc)}}{\ln N_{P=0}} \right] \quad (180)$$

Equation (180) results from our taking natural logarithms of equation (176) and solving for r_P. Now that we have determined values of r and f for $P_{(calc)}$, we can proceed to evaluate $S^2_{P_{(calc)}}$, the variance of a calculated P that exactly satisfies equation (176).

To evaluate the variance of $P_{(calc)}$, we employ equation (175) where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, r_P, and $f_{(calc)}$. The expression for these derivatives are given by equations (51), (52), (53), and (56).

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The variance of $Z_{P_{(calc)}}$, where $Z_{P_{(calc)}}$ is given by

$$Z_{P_{(calc)}} = 1 + BP_{(calc)} + CP^2_{(calc)} \quad (177)$$

and $P_{(calc)}$ is any calculated P which exactly satisfies equation (176), involves evaluation of the quantity

$$S^2_{Z_{P_{(calc)}}} = \sum_{r=1}^{n} \left(\frac{\partial Z_{P_{(calc)}}}{\partial P_{r(obs)}}\right)^2 S^2_{P_{r(obs)}} \tag{181}$$

where $S^2_{Z_{P_{(calc)}}}$ is the variance of $Z_{P_{(calc)}}$ and $S^2_{P_{r(obs)}}$ is the variance of $P_{r(obs)}$.

To evaluate equation (181), we evaluate $[\partial Z_{P_{(calc)}}/\partial P_{r(obs)}]$ for each $P_{r(obs)}$, multiply this quantity by $S_{P_{r(obs)}}$, square the product, and then sum the product over all of the observed P_r's. When we do this, we get

$$S^2_{Z_{P_{(calc)}}} = \left[\begin{array}{l} B^2 S^2_{P_{(calc)}} + 4C^2P^2_{(calc)} S^2_{P_{(calc)}} + P^2_{(calc)} S^2_B \\ + P^4_{(calc)} S^2_C + 4BCP_{(calc)} S^2_{P_{(calc)}} + 2BP_{(calc)} S^2_{B,P_{(calc)}} \\ + 2BP^2_{(calc)} S^2_{C,P_{(calc)}} + 4CP^2_{(calc)} S^2_{B,P_{(calc)}} \\ + 4CP^3_{(calc)} S^2_{C,P_{(calc)}} + 2P^3_{(calc)} S^2_{BC} \end{array}\right] \tag{182}$$

The covariance terms $S^2_{B,P_{(calc)}}$ and $S^2_{C,P_{(calc)}}$, which appear in equation (182), are defined as

$$S^2_{B,P_{(calc)}} = \sum_{r=1}^{n} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} \tag{183}$$

$$s^2_{C,P_{(calc)}} = \sum_{r=1}^{n} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right) s^2_{P_{r(obs)}} \tag{184}$$

and these quantities are to be evaluated from equations (183) and (184), which we proceed to do.

$[\partial P_{(calc)}/\partial P_{r(obs)}]$ can be determined from equation (174) where the terms involving derivatives of F are to be evaluated for $P_{(calc)}$, r_P, and $f_{(calc)}$. Multiplying equation (174) by $(\partial B/\partial P_{r(obs)}) s^2_{P_{r(obs)}}$ and summing the product over all of the observed P_r's, we get

$$\sum_{r=1}^{n} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial B}{\partial P_{r(obs)}}\right) s^2_{P_{r(obs)}} = s^2_{B,P_{(calc)}} = -\left[\frac{s^2_B\left(\frac{\partial F}{\partial B}\right)_{r_P,C,N_{P=0},P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N_{P=0}}} + \frac{s^2_{BC}\left(\frac{\partial F}{\partial C}\right)_{r_P,B,N_{P=0},P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N_{P=0}}} + \frac{s^2_{BN_{P=0}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r_P,B,C,P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P,B,C,N_{P=0}}}\right] \tag{185}$$

Multiplying equation (174) by $(\partial C/\partial P_{r(obs)}) S^2_{P_{r(obs)}}$ and then summing the product over all of the observed P_r's, we get

$$\sum_{r=1}^{n} \left(\frac{\partial P_{(calc)}}{\partial P_{r(obs)}}\right)\left(\frac{\partial C}{\partial P_{r(obs)}}\right) S^2_{P_{r(obs)}} = S^2_{C,P_{(calc)}} = - \left[\frac{S^2_{BC}\left(\frac{\partial F}{\partial B}\right)_{r_P, C, N_{P=0}, P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P, B, C, N_{P=0}}} + \frac{S^2_C\left(\frac{\partial F}{\partial C}\right)_{r_P, B, N_{P=0}, P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P, B, C, N_{P=0}}} + \frac{S^2_{CN_{P=0}}\left(\frac{\partial F}{\partial N_{P=0}}\right)_{r_P, B, C, P_{(calc)}}}{\left(\frac{\partial F}{\partial P_{(calc)}}\right)_{r_P, B, C, N_{P=0}}} \right] \tag{186}$$

Therefore, the use of equations (185) and (186) in equation (182) will enable the variance of a calculated Z_P, $S^2_{Z_{P(calc)}}$, to be determined.

In a following paper, the Helium Research Center will apply the equations developed in this report to some PVT data on helium at 0° C obtained by the Burnett method.

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